ROAST 2011

A. The climate penalty for clean fossil fuel combustion
W. Junkermann, B. Vogel, and M. A. Sutton
Atmos. Chem. Phys. Discuss., 11, 34567-34589, 2011

B. Climatic effects of 1950–2050 changes in US anthropogenic aerosols – Part 1: Aerosol trends and radiative forcing
E. M. Leibensperger, L. J. Mickley, D. J. Jacob, W.-T. Chen, J. H. Seinfeld, A. Nenes, P. J. Adams, D. G. Streets, N. Kumar, and D. Rind
Atmos. Chem. Phys. Discuss., 11, 24085-24125, 2011

C. Earth's energy imbalance and implications
J. Hansen, M. Sato, P. Kharecha, and K. von Schuckmann
Atmos. Chem. Phys. Discuss., 11, 27031-27105, 2011

D. A simple relationship between cloud drop number concentration and precursor aerosol concentration for the regions of earth's large marine stratocumulus decks
D. A. Hegg, D. S. Covert, H. H. Jonsson, and R. K. Woods
Atmos. Chem. Phys. Discuss., 11, 28663-28687, 2011

E. Indirect radiative forcing of aerosols via water vapor above non-precipitating maritime cumulus clouds
M. A. Pfeffer, J. E. Kristjansson, F. Stordal, T. Berntsen, and J. Fast
Atmos. Chem. Phys. Discuss., 11, 27637-27659, 2011

http://www.atmos-chem-phys-discuss.net/papers_in_open_discussion.html

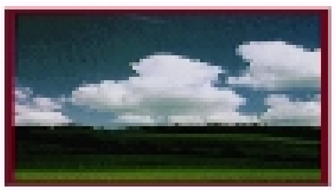
Lecture Ch. 5a

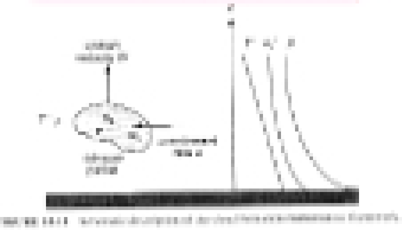
- Surface tension (Kelvin effect)
  - Hygroscopic growth (subsaturated humidity)
  - Saturation
- Chemical potential (Raoult effect)
- Nucleation
  - Competition between surface and chemical effects
  - Köhler curves
- Aerosol-cloud interactions

Curry and Webster, Ch. 5 (skip 5.6, 5.7); also 4.5.1
Optional: Pruppacher and Klett, Ch. 6
For Monday: Homework Problem 3 and 7 (Ch. 5) (7d misprint!)

Macro-Thermodynamics

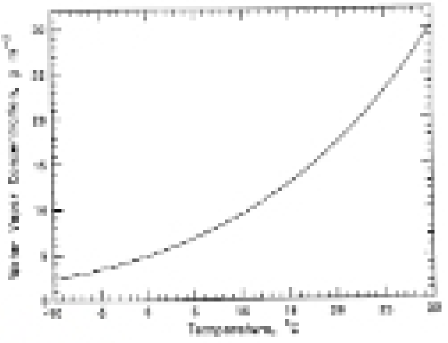
- Hot air rises
- Rising air cools
- Cooled moist air saturates
- (Sub & Super)-saturated water vapor condenses
- Condensation liberates heat





Water Saturation

- Saturation concentration of water over a flat water surface



Seinfeld and Pandis, Fig. 15.1

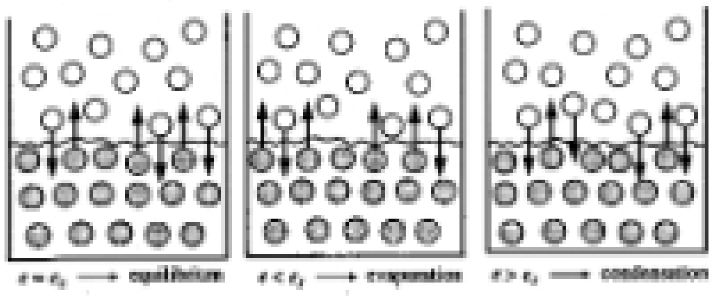


Figure 4.5 Schematic representation illustrating how the relative magnitudes of the vapor pressure of the water vapor layer, e and the saturation vapor pressure of the liquid below it, e_s determine the phase transitions between water and water vapor. When $e = e_s$, the vapor and liquid are in equilibrium and there is no net exchange between water and water vapor. When $e < e_s$, there is a net transfer of water into water vapor (i.e., net evaporation). When $e > e_s$, there is a net transfer of water vapor into water (i.e., net condensation).

N.B. Equilibrium is in but is NOT the same as "steady state."

Table 4.3 Coefficients of the sixth-order polynomial fits to saturation vapor pressure for the temperature range –50° to 50°C for both liquid water and ice. (After Flatau *et al.*, 1992.)

Coefficient	Liquid water	Ice
a_1	6.11176750	6.10952665
a_2	0.443986062	0.501948366
a_3	0.143053301E-01	0.186288989E-01
a_4	0.265027242E-03	0.403488906E-03
a_5	0.302246994E-05	0.539797852E-05
a_6	0.203886313E-07	0.420713632E-07
a_7	0.638780966E-10	0.147271071E-09

Micro-Thermodynamics

- Saturation has the most possible dissolved species
- Equilibrium means two phases are balanced
- Supersaturated states are not stable
- Nucleation initiates a change of "phase" (from particle to droplet)

Bohren, 1987

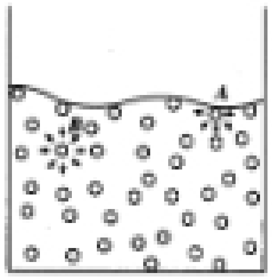
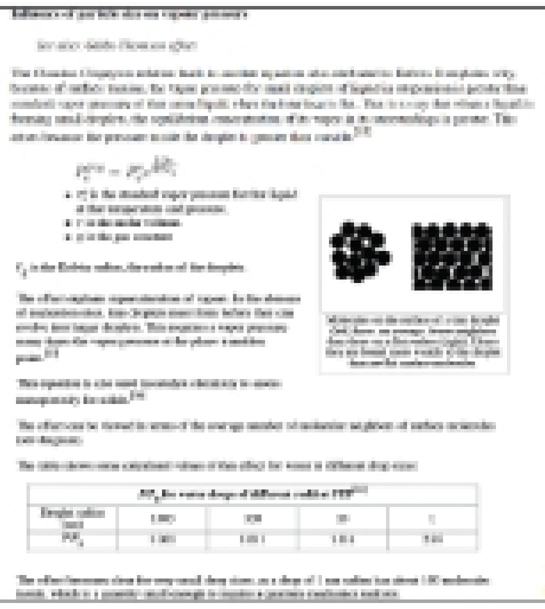


Figure 5.1 Water molecules at the surface of a liquid are subjected to a different attractive force field than those in the interior. A surface molecule, *A*, experiences a net attractive force towards the interior of the liquid. An interior molecule, *B*, experiences a symmetric force field exerted by its neighboring molecules and therefore does not freely move to the surface.



Influence of particle size on vapour pressure

Wikipedia, surface tension 10/20/09.

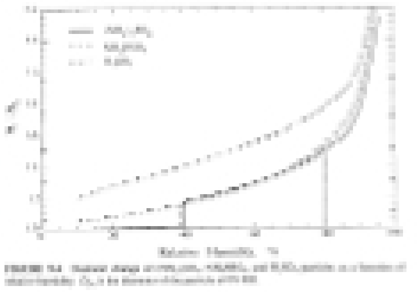
Surface Thermodynamics

- Surfaces require energy to form
- Smaller particles have
  - higher surface-to-volume ratios
  - higher curvature
- Higher curvature requires more energy per mass

$$S_{v,w} \equiv \frac{e_{a,w}}{e_{sat,w}} = \exp\left(\frac{4M_w\sigma_{w/a}}{RT\rho_w D_p}\right)$$

Hygroscopic Growth of Particles

- Normalized diameter change (growth factor) of sulfate species
  - Relative to particle size at 0% RH



Seinfeld and Pandis, Fig. 9.3

Free Energy Equation

- Surface energy

$$dW_s = \sigma\, dA \qquad (5.1)$$

$$dW_s = \sigma_s 8\pi r\, dr \qquad (5.3)$$

where σ_s is the surface tension between the liquid and vapor phases. Since the work

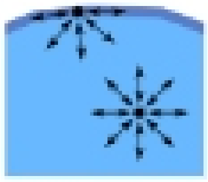
$$\sigma_s\, dA = \delta_{W}\, dW \qquad (5.4)$$

- Free energy at constant T, P

$$dG = -S\,dT + V\,dp + \sigma_s\, dA + \mu_l\, dn_l + \mu_v\, dn_v \qquad (5.5)$$

If we assume that nucleation occurs at constant temperature and pressure, and that $dn_l = -dn_v$, we have

$$dG = \sigma_s 8\pi r\, dr + (\mu_l - \mu_v)\, dn_l \qquad (5.9)$$



Kelvin Equation

- vapor pressure over a curved interface always exceeds that of the same substance over a flat surface
  - vapor pressure of a liquid – energy necessary to separate a molecule from the attractive force of its neighbors
  - curvature - increases the distance between a molecule and its neighbors so it has fewer neighbors -- therefore it is easier for molecules to break free
- for pure water Kelvin effects are important <0.05 µm diameter droplets

$$RH = \frac{P_w}{P_w^{sat}} = x_w \gamma_w \exp\left[\frac{4M_w \sigma_w}{RT\rho_w D_p}\right]$$

Ambient conditions

RH	relative humidity
T	temperature
P_w	vapor pressure
P_w^{sat}	saturation pressure

Particle composition

x_w	mole fraction of water
γ_w	activity coefficient for water
σ_w	surface tension of solution
ρ_w	density of aqueous solution
M_w	molecular weight
D_p	particle diameter

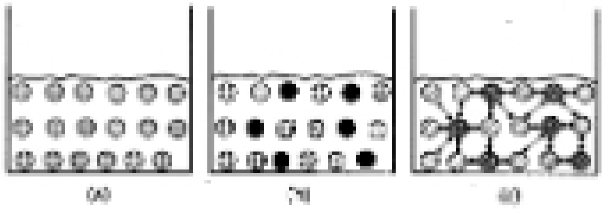


Figure 4.6 Schematic diagram illustrating the reduction in saturation vapor pressure in a solution. In (a) and (b), pure water molecules are represented by dotted circles, and nonelectrolytic molecules are represented by solid circles. The reduction in saturation vapor pressure in the solution (b) arises from the reduction in surface area occupied by the water molecules, since fewer water molecules are able to escape from the surface. In an electrolytic solution (c), both the solute (cross-hatched circles) and solution (hatched circles) become ionized, further reducing the saturation vapor pressure because of the attractive forces exerted by the solute ions on the water molecules.

Raoult's Law

4.5.1 Vapor Pressure Depression

Raoult's Law

electrolyte (NaCl). Raoult's law for dilute solutions was modified for dilute electrolytic solutions by van't Hoff, who found that an electrolytic solution effectively contains an increase in the number of moles of solute, so that

$$n_{solute}^{eff} = i n_{solute} \qquad (4.47)$$

where i is the van't *Hoff dissociation factor*. For strong electrolytic solutions, i is equal to the number of ions formed in solution; for weak electrolytic solutions it is less than this number but still greater than one. The ratio of the vapor pressure of a dilute electrolytic solution to that of pure water is thus

$$\frac{p_{sdw}}{e_s} = 1 - \frac{i n_{solute}}{n_{H_2O}} \qquad (4.48)$$

Since $i > 1$, it is seen that the partial pressure over an electrolytic solution is less than that of an equivalent nonelectrolytic solution. The reduction of vapor pressure for an electrolytic solution arises from the attraction between the highly polar water molecules and the ions (Figure 4.6c), which reduces the escaping tendency for the water molecules below that for a nonelectrolytic solution. For seawater with salinity of 35 psu (assuming $i = 2$), the saturated vapor pressure is $p_{sdw} = 0.98e_s$.

Chemical Potential

- From Maxwell's equations

$$\left(\frac{\partial g}{\partial p}\right)_T = v \qquad \left(\frac{\partial g}{\partial T}\right)_p = -\eta \qquad (2.48)$$

- Integrating from vapor to liquid

The term $(\mu_l - \mu_v)$ can be evaluated as follows. For an isothermal process involving one mole of water vapor, we can write

$$d\mu_v = dG = R^* T\, d(\ln e)$$

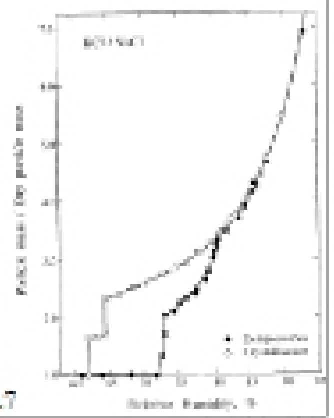
$$\mu_{v,l} = \mu_v^0 + R^* T \ln\frac{e_s}{e_0}$$

Since $\mu_l = \mu_{vl}$ when the two phases are in equilibrium over a plane surface, we can therefore write

$$\mu_l - \mu_v = R^* T \ln\left(\frac{e_s}{e}\right) \qquad (5.10)$$

Measured Hygroscopic Growth

- Particle balance for levitating particles (Tang et al., 1987)
- Growth compensated by change in electric field
- Deliquescence occurs at transition from dry to wet



Seinfeld and Pandis, Fig. 9.7